

since no link involving H or D is broken, the different zero point energies of the two isotopes will have only a second order effect, or none, as found. In the surface reaction, and the steady chain reaction, the rates depend, not upon simple branching, but upon initiation and propagation mechanisms, one or other of which must involve the activation or dissociation of H₂ or D₂. The different zero point energies will then give rise to different activation energies, and hence to different rates, in accordance with observation.

It appears, therefore, that the study of the behaviour of the heavy isotope brings, from a somewhat unexpected angle, an interesting confirmation of several matters connected with the mechanism of the reaction.

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¹ *J. Amer. Chem. Soc.*, **56**, 1251; 1934.

² *Proc. Roy. Soc.*, A, **141**, 29; 1933.

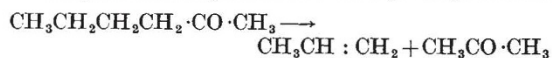
³ See Hinshelwood and Williamson, "The Reaction of Hydrogen with Oxygen" (Clarendon Press, 1934).

Photochemistry and Absorption Spectrum of Acetone

In a recent letter¹ we noted that the ultra-violet absorption band of acetone, which earlier workers² (with the apparent exception of Herzberg³) had regarded as continuous, has a fine structure. This occurs in the long wave side of the band; Bowen and Thomson⁴ now record a resolution of the remainder of the band into "about four groups each containing about 25 diffuse bands" but conclude that "the diffuseness of the bands can be attributed to an unresolved close packing of the rotation lines without calling on the additional hypothesis of pre-dissociation". In citing the fluorescence of acetone as evidence of the absence of dissociation, they make no reference to the fact that it is confined to the longer wave-lengths of the absorption band⁵. Actually the fluorescence disappears near the wave-length at which the line-structure noted by us becomes diffuse, and while this abrupt change can be readily explained by the onset of dissociation, it is not accounted for by the assumption that the diffuse region consists of close packed rotational lines.

For the photochemical decomposition of acetone Bowen and Thompson adopt the mechanism which we suggested for the decomposition of aldehydes⁶, namely, a unimolecular elimination of carbon monoxide according to the equation $R \cdot \text{CHO} \rightarrow \text{RH} + \text{CO}$. They make no reference, however, to the different behaviour of methyl ethyl ketone⁷, which gives a mixture of ethane, propane and butane in comparable quantities, instead of only propane. This crucial fact is not explained by the hypothesis which they have adopted, but is readily understood if the hydrocarbon chains are liberated as 'free radicals'.

The photodecomposition of methyl butyl ketone⁸:



is in complete contrast with that of acetone and was quite unforeseen by us; it would be of interest to know on what grounds these authors are able to regard it as "not unexpected". The initial electronic

excitation of the chromophoric group will undoubtedly be associated with various vibrations of the molecule, including the 'deformation' vibration mentioned by Bowen and Thompson, but in our opinion the energy associated with these vibrations is much too small to account for the decomposition of the butyl chain, which in the analogous case of butane requires an activation of 65 k. cal.⁷

It may now be suggested that the energy of excitation passes from the chromophoric group to another group within the polyatomic system by a process akin to the radiationless transfer in a collision of the second kind. This process, which we shall describe as 'inner sensitisation', need not give rise to a quantum yield of unity. In a complicated molecule there is likely to be a finite probability that the energy transfer may lead to thermal degradation instead.

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¹ Crone and Norrish, *NATURE*, **132**, 241, Aug. 12, 1933.

² See footnote in paper by Scheibe, Povenz and Lindström, *Z. phys. Chem.*, B, **20**, 297; 1933.

³ Scheibe and Lindström, *Z. phys. Chem.*, B, **12**, 387; 1931. Damon and Daniels, *J. Amer. Chem. Soc.*, **55**, 2363; 1933.

⁴ Bowen and Thomson, *NATURE*, **133**, 571, April 14, 1934.

⁵ Norrish and Appleyard, *Trans. Faraday Soc.*, **30**, 103; 1934.

⁶ Norrish and Kirkbride, *J. Chem. Soc.*, 1518; 1932.

⁷ Pease and Durgan, *J. Amer. Chem. Soc.*, **52**, 1262; 1930.

Chemistry of the Red and Brown Algae

SOME experiments of ours confirm the results of Dr. Russell-Wells on the presence of true cellulose in algae¹. From *Laminariae* we obtained cellulose from which we made viscose and which we converted into sugar by the method of Ost. This sugar gave phenylglucosazone, but no trace of insoluble phenylhydrazone (indicating mannose) was found.

We were led to these experiments by the well-known occurrence of mannitol in seaweeds and by the demonstration by Nelson and Cretcher² that algin is a polymerised uronic acid. Evidently, whatever uronic acid occurs in the plant, the unit of the cell wall material remains the same.

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¹ *NATURE*, **133**, 651, April 28, 1934.

² *J. Amer. Chem. Soc.*, **51**, 1914; 1929.

Phosphorescent Beryllium Nitride

ALUMINIUM nitride activated by silicon¹, and boron nitride activated by carbon², are the only known phosphorescent nitrides.

Phosphorescent beryllium nitride has been obtained by me by passing ammonia gas at 1,000° C. for four hours over a mixture of beryllium metal containing ten per cent alumina. The product thus obtained shows blue luminescence after exposure to a mercury arc lamp.

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¹ E. Tiede, Max Themann and K. Senses, *Ber.*, **61B**, 1568; 1928.

² E. Tiede and F. Buecher, *Ber.*, **53B**, 2206; 1920. E. Tiede and H. Tomaschek, *Z. Elektrochem.*, **29**, 303; 1923. E. Tiede and Heuriette, *Z. anorg. Allgem. Chem.*, **147**, 111; 1925.